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Study of the Formation and Transport of Acidic Species by Non-Precipitating Cumulus Clouds During VENTEX-84

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A STUDY OF THE FORMATION AND TRANSPORT OF ACIDIC SPECIES BY NON-PRECIPITATING CUMULUS CLOUDS DURING VENTEX-84

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INTRODUCTION

Satellite photographs show that, at any one time, approximately half of the earth's surface is covered by clouds. However, it has been estimated that less than one tenth of this cover can produce precipitation (McDonald 1958). This means that more than 90% of the cloud cover evaporates and may form clouds at a later time. If we assume that the cloud cover thickness is 3.0 km and the liquid water content of the cloud is 0.5 g/m^3, then the average liquid water over the earth's surface is 1.5 kg/m^2. Because the global average precipitation is about 1 m/year (Sellers 1974), the average residence time of liquid water is about 13 hours. However, the average lifetime of a cloud is much shorter than that, approximately in the range of 30 minutes to 1 hour (Pruppacher and Klett 1978). Therefore, the clouds must go through approximately 13 to 26 cycles of condensation and evaporation before their water reaches the ground. During cloud formation, atmospheric aerosols and gases are incorporated in the cloud droplets and may undergo chemical and physical changes before they are reemitted to the atmosphere. Possible changes are the formation of new aerosol particles by the aqueous phase chemical reaction, and the modification of the aerosol size distribution. These changes do influence the rates of wet and dry removals of the pollutants from the atmosphere and their impact on man.

During the warm season its very common to see non-precipitating cumulus clouds covering a substantial portion of the visible sky. The National Weather Service observational record for the period from 1978 to 1981 shows that these clouds were present over Lexington, KY approximately 17 days in each month of June, July, and August (Alkezweeny 1984). Plank (1969) reported that the total volume of a typical sky cover over Florida peaks around midday. Furthermore, the ratio of this volume to the volume of the boundary layer below, calculated from his data, is between 0.3 and 0.4 for the time period 1100 to 1500[(a)]. Over Lexington, KY this ratio varies over a wider range from one day to the other but the averaged value is in this given range. Since the clear air first order transformation rate of sulfur dioxide to sulfate is less than 5%/hour and also peaks around midday (Calvert and Stockwell 1983),

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(a) All times reported in this report are in eastern daylight time.

and as will be seen later that the in-cloud conversion rate can be much higher. Therefore the presence of these clouds contributes significantly to the sulfate, and possibly nitrate, levels in the atmosphere.

Since cumulus clouds form by convective activities that originated near the surface, they transport pollutants to the cloud layer. Later in the afternoon, when the clouds evaporate and vertical mixing is poor, a layer of pollutants may exist and can be transported horizontally to other regions. Distance transport is also possible if the clouds penetrate into the stable free atmosphere above the mixed layer evaporate by mixing with the dry air and the residue can be carried away by the wind which is generally high at those elevations.

This report is the second in a series of reports that describes the VENTEX field studies conducted near Lexington, KY. The first one was published by Alkezweeny (1984). In this report, description of the experiment conducted during the summer of 1984 (VENTEX-84), from July 8 to August 18, will be presented, and samples of the data collected will be given. Possible uses of the data and example of data manipulation will be illustrated.

OBJECTIVES

The principal objectives of this program are as follows:

- to determine the production of sulfate and nitrate aerosol particles by non-precipitating cumulus clouds
- to investigate the vertical transport of pollutants caused by cumulus convection

SCOPE

The basic scope of this project is to generate a large data base comprehensive enough for the development and validation of a cloud chemistry and vertical transport modules for the non-precipitating clouds. This will be accomplished through field studies and data interpretation. Statistical

analysis of the data will also be carried out to study the transformation and transport.

PREVIOUS WORK

CLOUD CHEMISTRY

It has been established that dissolved sulfur dioxide can be oxidized to form sulfate in liquid water. The rate of oxidations by ozone and hydrogen peroxide have been measured (Maahs, 1983; Martin and Damschen, 1981). On the other hand, observations of sulfate formation in natural clouds are very limited. The first observation was reported by Alkezweeny and Hales (1981). Using instrumented aircraft, Alkezweeny and Hales collected aerosol samples at bases and tops of non-precipitating cumulus clouds and analyzed for sulfur and trace metal content of the aerosols. Since in similar type of clouds the majority of inflow and outflow are at cloud bases and tops respectively, a comparison between aerosols measured in the two sites may be an indication of aerosol formation. Furthermore, aerosols emerging from cloud tops are diluted because of mixing with dry clean air above the mixed layer, therefore, the concentration needs to be normalized by a conservative tracer (a tracer that does not change chemically during its residence in clouds). The element Fe and K were chosen and the normalized concentrations are given in Table 1. It can be seen that the concentrations at cloud tops are higher than cloud bases. The increases on July 17 are not significant and fall within the measurement error, which indicates that sulfate did not form on this day, either because of a lack of sulfur dioxide in the air entering the clouds or some other reason such as a lack of oxidant. On the other hand, definite sulfate formation is shown in the July 19 data; clearly the increases in the concentrations are much larger than measurement errors. Unfortunately, they did not measure sulfur dioxide needed in order to estimate the oxidation rate.

Sulfate formation has also been detected in wave clouds by Hegg and Hobbs (1982). They found that the conversion rates of sulfur dioxide to sulfate to be variable, and the rate can be as high as 300%/hr. When power plant plume interacted with a cloud, Gilliani et al. (1983) estimated that the average rate

was (12 ± 6)% /hr for a midsummer day. Similarly, Eatough et al. (1984) deduced an average rate of (25 ± 4)% /hr when an oil-fired power plant plume passed through a fog bank.

TABLE 1. Comparison between the normalized concentrations of sulfur aerosols measured at the cloud inflows (cloud bases) and the outflows (cloud tops), indicating sulfate production. Data are from Alkezweeny and Hales (1981).

DATE	POSITION	S/Fe	S/K
7/17/79	CLOUD BASES	4.9 ± 0.7	7.8 ± 1.3
	CLOUD TOPS	6.0 ± 1.2	9.7 ± 2.5
7/19/79	CLOUD BASES	6.0 ± 1.1	13.6 ± 2.8
	CLOUD TOPS	28.0 ± 4.0	41.0 ± 6.5

VERTICAL TRANSPORT

Experimental studies of the vertical transport by cumulus activities started only a few years ago, and are mostly qualitative in nature. In one experiment, Alkezweeny and Hales (1981) made a constant altitude sampling flight above a field of non-precipitating cumulus clouds over Illinois and detected boundary layer aerosols and trace gases when the aircraft passed over a cloud. Ching et al. (1983) made several penetrations by instrumented aircraft through cumulus clouds over southeastern Pennsylvania and measured ozone concentrations 10 to 15 ppb higher than the concentrations outside the clouds at the same elevation. Based on analysis of several vertical profiles of Radon 222, an inert gas of continental ground origin, Liu et al. (1984) estimated that 55% of the Radon 222 in summer was transported out of the mixed layer. Isaacs et al. (1983) carried out preliminary analyses of their data and estimated the rates of volume of subcloud air pumped through the cloud to the total volume of the subcloud layer to be 50%/hr in the summer and 20%/hr during other seasons. During VENTEX-83, SF_6 tracer was released on two occasions within the mixed layer, just below cloud bases, and on another occasion at tops of a field of active clouds. Samples were taken both on and above the ground (Alkezweeny 1984, Ching and Alkezweeny 1985). When all samples were analyzed the following picture emerged: pollutants are carried upward to the cloud layer by thermal plumes or cloud updrafts. The cloud layer

consists of fair weather cumulus clouds, and towering clouds in various stages of their growth. The towering clouds penetrate deep into the free atmosphere and when they evaporate they leave the transported material aloft. The detrainment occurs primarily at and above the cloud top. On the other hand, the downdrafts associated with these clouds bring free tropospheric air into the mixed layer and ultimately to the ground. Niewiadomski (1986) used a three-dimensional cloud model to investigate the vertical transport of pollutants by a field of non-precipitating cumulus clouds. Based on his numerical simulation, he concluded that a field of relatively weak and sparse cumuli can in one hour reduce the average boundary layer pollutant content by 15%.

FIELD EXPERIMENT

The VENTEX-84 field program was conducted near Lexington KY during the period July 8 to August 18. The field activities involved several research groups, and consisted of ground sampling and aircraft sampling in the clouds and their environment. A summary of these activities is shown in Figure 1. These groups are: Pacific Northwest Laboratory (PNL), Argonne National Laboratory (ANL), Research Triangle Institute (RTI), and Kentucky Center for Energy Research Laboratory (KCERL). Physical characteristics of clouds were determined by RTI using a laser finder and photography. Basic boundary layer parameters such as heat fluxes, height of the mixed layer top, vertical profiles of temperature and relative humidity, and wind speed and direction at the ground were obtained daily by ANL. KCERL provided logistical support and carried out chemical analyses of exposed filters. The PNL contribution consisted of two instrumented aircraft, ground sampling of aerosols and trace gases, and releases of radiosondes. Details of the PNL activities will be described below under subsections cloud chemistry and vertical transport.

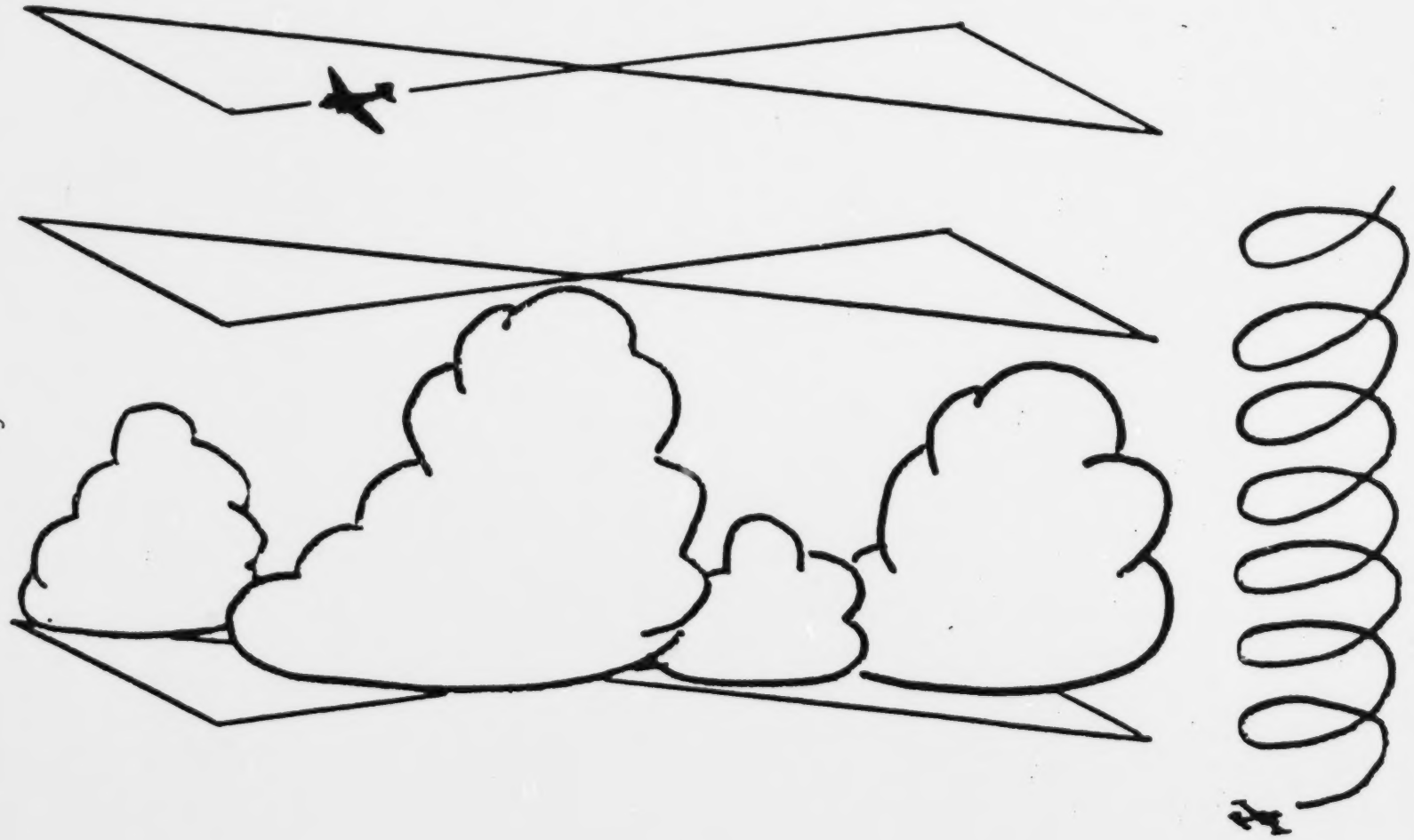

FIGURE 1. Aircraft flight paths to characterize the cloud environment.

CLOUD CHEMISTRY

Samples of aerosols and trace gases were collected above the mixed layer in cloud-free air (background samples), generally above 3,000 m[(a)], at the cloud inflow region (cloud bases) and cloud outflow region (cloud tops) using the PNL DC-3 aircraft. The background samples were needed because when clouds penetrate into the free atmosphere above, they mix with dry air and evaporate; thus, the samples taken at the cloud outflow must be corrected for the background concentrations. The aircraft flight routes consisted of a constant altitude bow-tie path with one leg of the flight path passing over the VENTEX ground sampling site (Figure 1). Several parameters were measured in real-time; these are: O_3, SO_2, NO_x, aerosol light scattering, aerosol size distribution, temperature, dew point temperature, altitude, turbulence in the inertial subrange, and aircraft position. The aircraft was equipped with two high-volume samplers. Each sampler used a filter pack that exposed 21.2 cm^2 of the filter area. One filter pack consisted of a Teflon® filter for the collection of aerosols, followed by a cellulose filter impregnated with sodium chloride for nitric acid collections, followed by another cellulose filter impregnated with potassium carbonate and glycerine for sulfur dioxide collections. The second filter pack employed a Teflon® filter, backed by a cellulose filter treated with oxalic acid for the collection of ammonia gas.

As part of the surface-level sampling, two filter packs were used to measure the chemical composition of aerosols and to monitor the concentrations of sulfur dioxide and ammonia gas.

At the beginning of filter sampling an identical filter pack was handled but not exposed and later analyzed in the same manner as the filter pack that is being exposed in the high-volume sampler, so that filter blank and contamination corrections can be made. Each exposed filter was placed inside a 50 ml plastic syringe which contained distilled deionized water and left for 24 hours, transferred to 60 ml plastic bottles, and analyzed. This filter extraction technique was checked at PNL chemistry laboratory and found to be more than 95% efficient in extracting water soluble compounds. The extracted

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(a) All altitudes reported in this report are above sea level.
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solutions of the exposed and blank teflon filters were checked for conductivity and pH, and then analyzed for anions and cations. Table 2 lists the methods of analyses and the detection limits of the technique for each species. Nitric acid and sulfur dioxide were determined as nitrate and sulfate ions by the ion chromatography method. Ammonia was determined as ammonium ions by the Automated Wet Chemistry (Colorimeter) technique.

VERTICAL TRANSPORT

The vertical transport was studied using two instrumented aircraft, the PNL DC-3 and Cessna 411. The DC-3 was outfitted with a gust probe and inertial navigation system for measurement of wind velocity and turbulence in real-time. The data were made simultaneously with the cloud chemistry measurements described above; thus, making it possible to determine fluxes of pollutants at cloud bases and tops.

The Cessna 411 aircraft was instrumented to measure temperature, dewpoint temperature, ozone, light scattering, altitude, and aircraft position. The aircraft flew twice during the day and obtained the vertical profiles of these species from an altitude of 600 to 3,600 m, two to three times per flight. The aircraft also made several passes through cloud tops.

In support of the aircraft flights, wind speed and direction, temperature, and relative humidity were measured at midday by means of radiosonde. Furthermore, vertical profiles of temperature, and dewpoint temperature were also obtained twice a day by ANL from the releases of airsondes.

TABLE 2. Techniques and detection limits for anion and cation analyses

Species	Technique	Detection Limit
Cl^-	IC	0.14 μmol/l
NO_3^-	IC	0.16 μmol/l
$SO_4^=$	IC	0.31 μmol/l
Na^+	IC	0.22 μmol/l
NH_3^+	IC	0.55 μmol/l
K^{++}	IC	0.77 μmol/l
Ca^{++}	DCP	0.75 μmol/l
Mg^{++}	DCP	0.21 μmol/l

IC = Ion Chromatography
DCP = Direct Coupled Plasma Spectrophotometer

DATA MANAGEMENT

The aircraft data were collected on magnetic tapes, strip chart recorder and aircraft flight scientist notes. The DC-3 carried two data acquisition systems, an HP-9920 computer-based system and a Particle Measuring DAS-64 system. The later one was used as a back up and recorded most of the real-time parameters with the exception of the Gust Probe and the INS data. Both systems record the data on 9-track tapes. The data acquisition onboard the Cessna 411 aircraft was also a computer-controlled system that recorded the data on 1/4-inch magnetic tape cartridges.

The data reduction process involves the merging of the data sets, along with appropriate calibration information, to create a reduced data tape in engineering units with all corrections for invalid or unwanted intervals edited and data formatted. The reduced data tape is written in ASCII for ease of interpretation and processing at various computer facilities. The tape also contains a first file of header information that includes the flight dates, tape recorded size, the order of parameters, and the format statement used to write the parameters.

RESULTS AND DISCUSSION

In the following sections samples of the data collected will be presented and discussed. Since the bulk of the data has not been examined any conclusion drawn from these limited data should be viewed as highly tentative.

CLOUD CHEMISTRY

Table 3 shows the concentrations of sulfate, sulfur dioxide, nitric acid, and nitrate measured at three altitudes each day. The lowest altitude was chosen just below cloud bases, the intermediate altitude was at cloud tops, and the higher altitude was much higher than cloud tops. The concentrations of each species, at any altitude, varied from one day to another without any particular trend or correlations among them. Nitric acid concentrations are much higher than nitrate aerosol concentrations with the exception of one

data point taken at cloud bases on July 31. In some cases the nitric acid concentrations are higher than sulfate concentrations. For example, on August 4 the concentration of nitric acid is 22.9 nmoles/m^3 compared to only 0.2 nmoles/m^3 at cloud bases. There was a similar trend at the two other altitudes and also on days August 8 and 12.

TABLE 3. Data collected during VENTEX-84 by the PNL DC-3 aircraft at bases, tops, and higher than tops of non-precipitating cumulus clouds. Altitudes are in thousands of meters, and the concentrations of SO_4, SO_2, HNO_3, and NO_3 are in nanomoles/m^3. Times are in eastern daylight time.

DATE	ALTITUDE	TIME ON-OFF	SO_4	SO_2	HNO_3	NO_3^-
7/30	1.1	1250-1335	31.3	7.7	20.7	0.0
	1.8	1350-1450	61.1	2.0	20.3	1.3
	3.1	1132-1230	18.6	1.7	8.9	0.0
7/31	1.4	1358-1443	20.9	8.2	2.1	11.2
	2.2	1455-1555	3.0	0.2	4.1	2.8
	3.1	1230-1330	0.6	0.0	2.3	0.0
8/04	1.1	1316-1346	0.2	44.2	22.9	0.0
	2.4	1404-1504	1.2	0.0	6.3	0.7
	3.1	1149-1249	0.0	0.0	4.1	0.0
8/08	1.1	1336-1421	21.7	67.7	54.2	1.5
	2.0	1439-1539	13.5	5.0	35.7	0.4
	2.4	1543-1643	1.5	0.0	20.5	0.3
8/12	1.4	1326-1412	51.1	237.5	76.5	1.1
	2.2	1432-1532	9.8	4.0	33.1	0.0
	3.1	1150-1250	0.0	0.0	0.0	0.0

The in-cloud formation of sulfate and nitrate are examined by comparing the concentrations at cloud tops against the concentrations measured at cloud bases. However, before this comparison can be made we must recognize that when cumulus clouds penetrate into the free atmosphere above the mixed layer, they encounter dry and less polluted air of different chemical composition, they mix with it, and evaporate. Thus the pollutants emerging from the clouds will be diluted and chemically modified. In Table 4 the concentrations of sulfate and total nitrate at cloud bases were divided by the total sulfur (the sum of sulfate and sulfur dioxide), and the values at cloud tops were first corrected for background values and then divided by the total sulfur at

that altitude. The nitric acid and the nitrate aerosols were combined because when ammonium nitrate and sulfuric acid dissolve in the droplet and the droplet evaporates, an exchange of ions takes place resulting in the formation of nitric acid and ammonium sulfate.

Table 4 includes the concentrations of ammonia and ozone, and outside air temperature. Since these parameters were measured in real-time, their values were averaged over filter collection time. The letters B and T refer to the measurements locations, at cloud bases and cloud tops respectively.

Examining the data in Table 4, it can be seen that the ratio of sulfate to the total sulfur at cloud tops is higher than that at cloud bases in all five days, and the changes in the ratio is much larger than the estimated combined errors in the measurements. This finding is in agreement with the VENTEX-83 results (Alkezweeny et al. 1984). In the case of total nitrate, three days (August 4, 8, and 12) show in-cloud nitrate formation. The other two days no production was detected. This is the first time that nitrate formation in natural clouds has been observed.

TABLE 4. Ratios N/S and SO_4/S at cloud bases, B, and cloud tops, T, where N is the concentration sum of nitric acid and nitrate aerosols, and S is the sum of sulfate and sulfur dioxide concentrations. k is the first order oxidation rate of SO_2 in clouds in %/minute. The ammonia and ozone concentrations are in nanomoles/m^3 and ppb respectively, and the temperature, T is in °C.

DATE	HEIGHT	N/S	SO_4/S	k	NH_3	O_3	T
7/30	B	0.53 ± .07	0.80 ± .02	15.0	4.6	60	19.1
	T	0.27 ± .04	0.99 ± .01	1.0		56	16.3
7/31	B	0.46 ± .01	0.72 ± .03	9.9	11.7	40	20.3
	T	1.77 ± .12	0.92 ± .01	6.5		27	14.3
8/04	B	0.52 ± .07	0.005 ± .00	10.9	15.2	57	22.6
	T	2.39 ± .31	1.00 ± .00	3.3		48	14.4
8/08	B	0.62 ± .08	0.24 ± .03	6.7	52.3	81	24.9
	T	0.90 ± .11	0.71 ± .03	20.4		66	19.6
8/12	B	0.27 ± .03	0.18 ± .02	8.0	5.0	78	20.2
	T	0.24 ± .30	0.71 ± .03		--	68	16.8

The oxidation rate of sulfur dioxide in the cloud system can be estimated in the following manner. Let the concentrations of sulfur dioxide and sulfate be represented by X and Y respectively. Therefore the time rate of changes in X and Y are:

$$dX/dt = -kX - KX \tag{1}$$

$$dY/dt = kX - KY \tag{2}$$

where k is the oxidation rate of SO_2, and K is the reduction rate due to dilution and diffusion. Define a descriptor R such that:

$$R = X/(X+Y) \tag{3}$$

Differentiating both sides of equation (3) with respect to t, and substituting for the time derivatives from equations (1) and (2) results in the following equation:

$$dR/dt = -kR \tag{4}$$

k is influenced by many processes. It includes the reaction rate between SO_2 and the oxidizers, functions that take into account the transfer of the gases from the air to the cloud droplets, and the concentrations of the oxidizers. Temperature changes as droplets rise from cloud bases to cloud tops will affect the value of k. For diagnostic analysis it is assumed that k is constant with respect to t, X, and Y. Integrating equation (4) yields the following:

$$kt = \ln R_0 - \ln R \tag{5}$$

where R_0 is the descriptor value at t = 0, at cloud bases.

In order to calculate k, the transport time t between cloud bases and cloud tops is needed. Assuming an average updraft velocity of 1.0 m/s across the cloud, the calculated values of k are shown in Table 4. The result shows very fast conversion rates. It should be noted that even if the updraft velocity is off by a factor of two or three the rate is still very high. Furthermore, the calculated rate varies from one day to the other and does not seem to correlate with any of the parameters listed in the table. Of course what is missing from the data is a measurement of H_2O_2. This measurement was not taken during VENTEX-84 but was made during VENTEX-85. Although the VENTEX-85 data have not been analyzed, preliminary examination show that the concentration of H_2O_2 is in the range of 1.0 t0 6.0 ppb; certainly large enough

to oxidize dissolved SO_2 in the cloud droplets. Furthermore, there is a strong indication that H_2O_2 was forming in the clouds. This was evident from vertical profiles which show peaks in the concentrations at the cloud layer.

The high SO_2 oxidation rates calculated above are consistence with VENTEX-83 results (Alkezweeny et al. 1984, c.f. Table 5) and those reported by Hegg and Hobbs (1982) for wave clouds. Model simulation of non-precipitating clouds by Seigneur and Saxena (1984) arrived at an oxidation rate on the order of 100%/hr. Martin and Damschen (1981) used their laboratory measurement of the aqueous oxidation of sulfur dioxide by hydrogen peroxide and calculated a rate of 3.0 %/min. for clouds containing 0.3 g/m^3 liquid and gas phase H_2O_2 concentration of only 1.0 ppb.

The rates reported here are higher than those measured by Gillani et al. (1983) and Eatough et al. (1984) for power plant plumes embedded in clouds. Although these authors did not report any hydrogen peroxide measurements, it can be assumed that in those studies the H_2O_2 concentrations were very low. Hydrogen peroxide vertical profile measurements during VENTEX-85 show that the peroxide concentration drops almost to zero when a plume containing high concentration oxide of nitrogen was encountered. This explanation is supported by the measurement of Clark et al. (1984). They measured the chemical composition of cloud water when a power plant plume was entirely trapped within a shallow layer filled with stratocumulus clouds. When they compared their measurements with the predictions of a reactive plume model they found the rates of sulfur dioxide oxidation outside the plume to be substantially higher than those within the plume. Since NO_x concentration is much higher at the plume center than at the plume edges, it follows that H_2O_2 concentration inside the plume should be very low.

Measurements taken during the VENTEX-83 field study have been used in model studies to simulate the chemistry system of the pollutants in a non-precipitating cumulus cloud (Nair et al. 1985). Since H_2O_2 data were not collected during that study, H_2O_2 concentration of 1.0 and 5.0 ppb were assumed; these concentration values are in the range of values measured near the clouds during the VENTEX-85 field study. The model result and the experiment values are given in Table 5 and are in reasonable agreement, considering the many assumptions made about liquid water content, cloud droplet sizes, etc. In

VENTEX-85 all the variables needed for this model simulation have been measured. Therefore, the data can be used for cloud chemistry model validation.

TABLE 5. Comparison between measured and simulated of SO_2, NH_3, and k. Data from Nair et al. (1985)

	SO_2 (nmoles/m^3)			NH_3 (ug/m^3)			k(%/min.)		
	Expt.*	1ppb**	5ppb**	Expt.*	1ppb**	5ppb**	Expt.	1ppb**	5ppb**
7/28	54.3 5.1	15.00	5.1×10^{-4}	0.108 0.000	7.8×10^{-4}	7.8×10^{-4}	5.0	4.1	28.0
8/02	14.7 0.1	0.89	0.079	0.375 0.011	0.019	0.020	36.0	27.0	51.0
8/08	78.2 12.8	46.00	5.10	0.080 0.003	7.7×10^{-4}	4.1×10^{-4}	2.0	4.2	21.0
8/19	202.0 0.9	155.00	57.00	0.230 ----	0.016	6.4×10^{-4}	16.0	2.1	9.8

*First number measured at cloud bases, and the second number measured at cloud tops.
**Assumed gas-phase H_2O_2 concentration

Results of the ground measurements reveal interesting features. In general the ammonia concentration profiles show a decline in concentration around midday followed by an increase in the afternoon. A typical ammonia profile taken on August 12 is given in Figure 2. On the other hand, the sulfur dioxide profiles peak around noontime (Figure 3). The ammonia behavior is expected since its sources are located on the ground. At night and early morning the ammonia is emitted into and confined within a shallow layer that is capped by the nocturnal temperature inversion. As the day progresses the inversion height rises and the ammonia is mixed and distributed over a deeper layer. In the late afternoon mixing is suppressed and therefore the concentration rises. More ammonia measurements taken in 1983 at the same location on the ground and at several elevations above the ground were reported by Alkezweeny et al. (1986). The sulfur dioxide profile suggests that the main source of SO_2 was an elevated plume. The weak or absence of vertical mixing during the afternoon, nighttime,

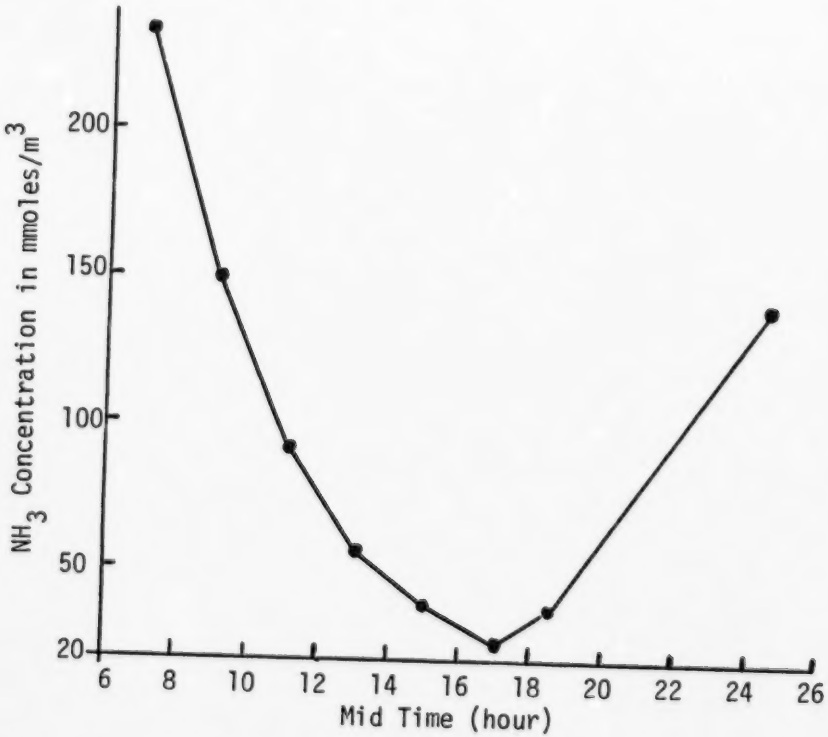

FIGURE 2. Ammonia concentrations measured on the ground near Kentucky Center for Energy Research Laboratory in Lexington, KY, August 12, 1984.

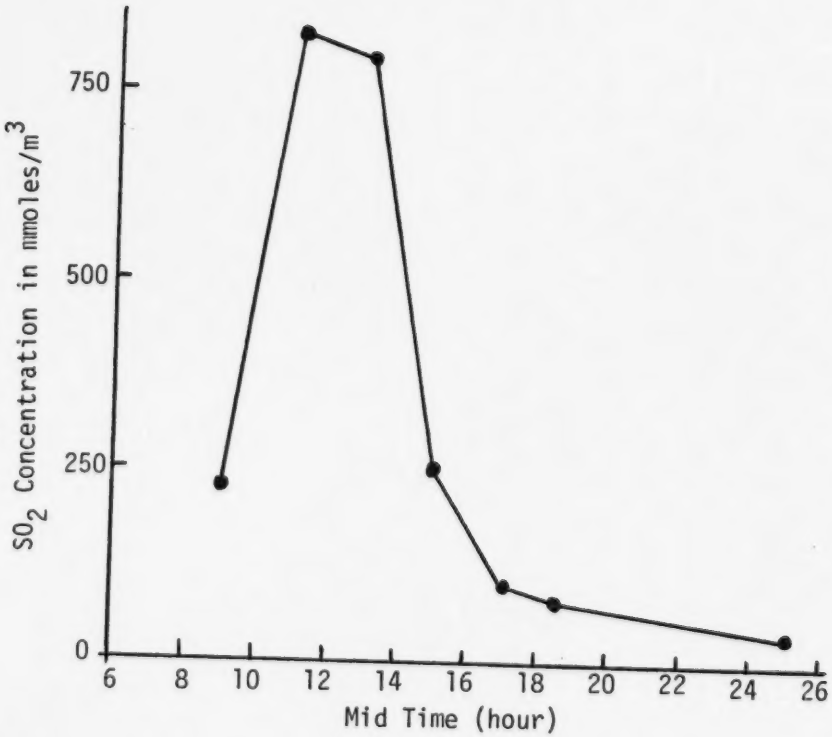

FIGURE 3. Sulfur dioxide concentrations measured on the ground near Kentucky Center for Energy Research Laboratory in Lexington, KY, August 12, 1984.

and early morning keep the concentration low. However, at midday, when mixing is at its best, the plume will be mixed to the ground and rise in the SO_2 concentration is expected.

VERTICAL TRANSPORT

Pollutant fluxes and other data collected by the PNL DC-3 aircraft instrumentation have not been analyzed. Data collected by the PNL Cessna-411 aircraft instruments are partially analyzed; examples of the results will be presented here. Figure 4 and 5 show the results of the aircraft constant altitude penetrations through cloud tops on July 13, 1984 during the morning and afternoon flights. Aircraft speed during penetrations was approximately 72 m/sec. An individual cloud is identified by the rise in the relative humidity trace. Peak values vary from one cloud to the other because as the cloud penetrates into the free atmosphere above the boundary layer, it mixes with the dry air and starts to evaporate, thus the relative humidity drops below saturation. The amount of reduction in the relative humidity, as detected by the sensors, depends upon the aircraft location within the cloud.

The temperature inside the cloud is 1 to 3°C lower than the cloud environment, at the same elevation, which is an indication of the cloud droplet evaporation.

The figures show ozone concentrations and aerosol light scattering inside the clouds are higher than that outside at the same elevation. The difference in the ozone concentration is in the range of 5 to 15 ppb, which is comparable with the 10 to 15 ppb measured by Ching et al. (1983) during their cloud penetration experiment. Alkezweeny and Hales (1981) also detected boundary layer ozone and other pollutants just above the visible cloud tops during aircraft sampling over clouds that formed near Champaign, Ill. It is interesting to compare the ozone concentration baseline measured during the morning and the afternoon flights. In the morning the concentration values vary from about 49 to 53 ppb and in the afternoon the range is 52 to 60 ppb. Since these measurements were taken above the mixed layer, the results suggest an accumulation of ozone, and possibly other pollutants, in the cloud layer (including the entrainment layer).

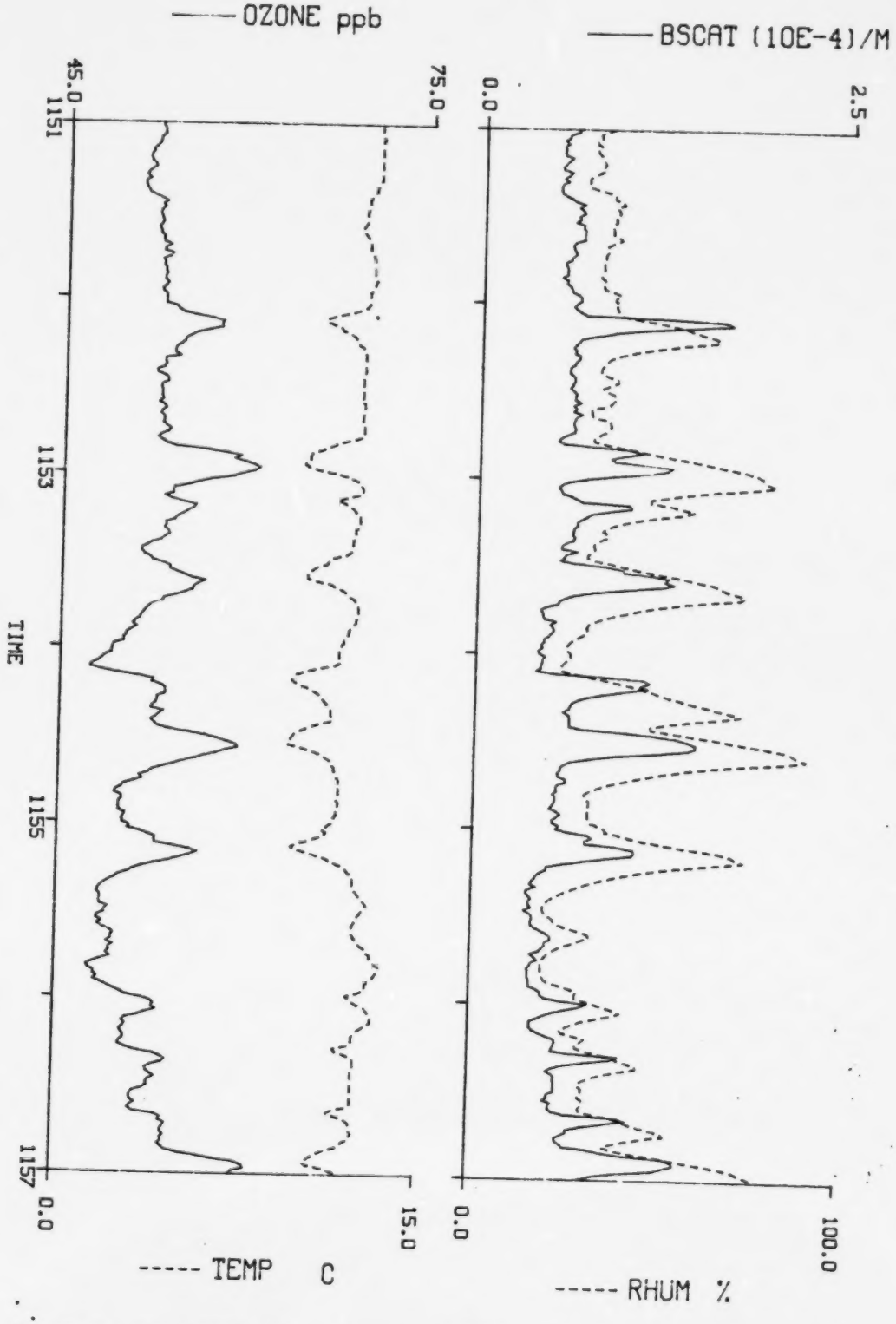

FIGURE 4. Cross sectional data of ozone, light scattering, relative humidity, and temperature derived from the aircraft penetrations, at constant altitude, through cloud tops on the morning of July 13, 1984.

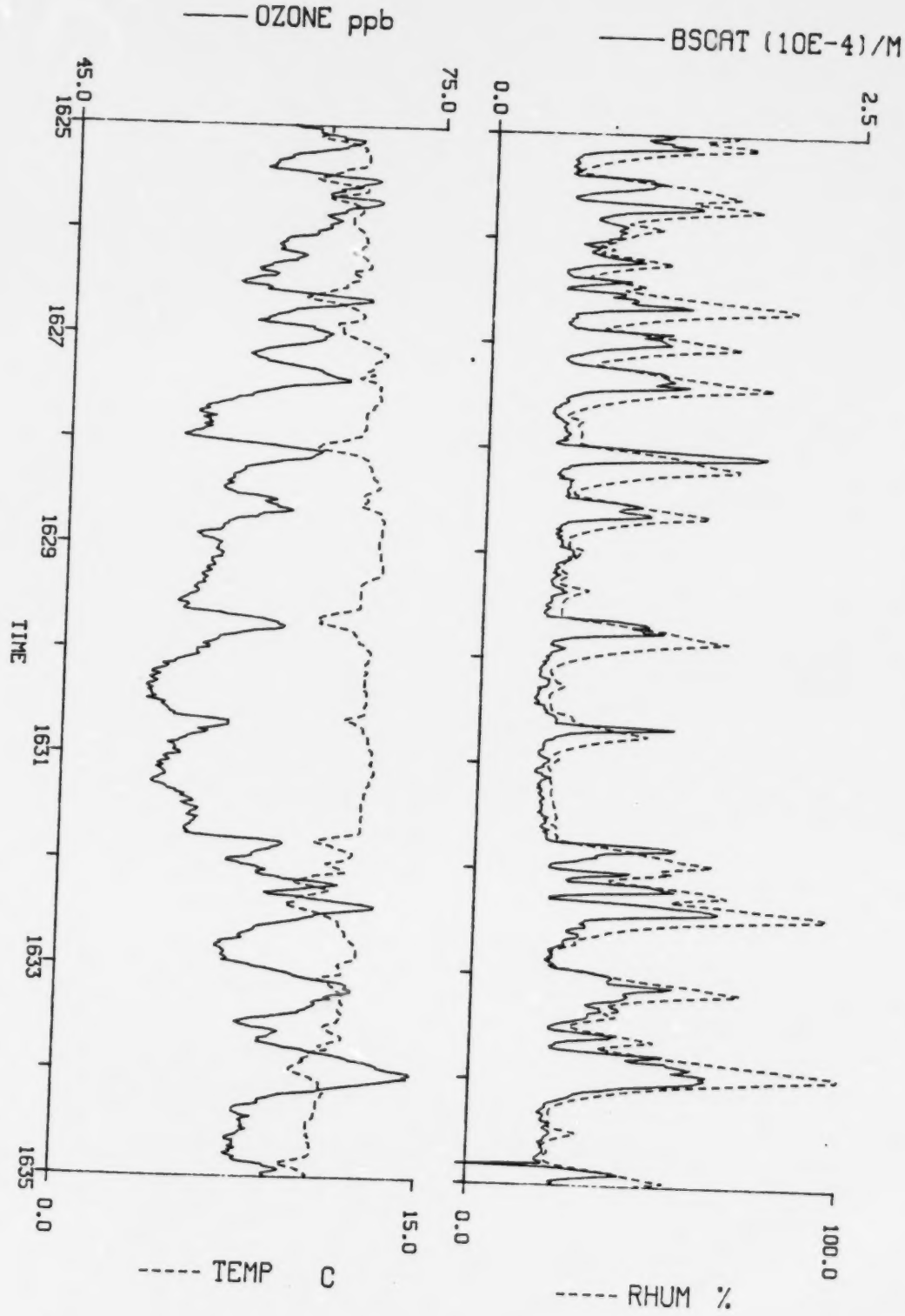

FIGURE 5. The Same as Figure 4 Except the Data were Collected in the Afternoon.

The vertical profiles of ozone, and temperature for the morning and afternoon flights on July 13, 1984 are given in Figures 6 and 7. At 1130 the top of the mixed layer was at about 1900 m. Cloud bases were estimated at 1800 m and most of the cloud tops were at 2000 m. By 1645 the top of the mixed layer had risen to 2300 m, cloud bases to 2250 m, and cloud tops to 2500 m. Below the cloud layer the ozone concentration increased at all altitudes by approximately 20 ppb over the five-hour period presumably as a result of photochemical reaction expected to take place in polluted atmosphere. The rate of increase, 4 ppb per hour, is comparable with the values of 5 to 10 ppb per hour reported by Alkezweeny et al. (1980) in polluted air over Lake Michigan during the afternoon hours. Above about 2600 m the ozone concentration was practically unchanged during this period, which suggests that vertical transport, if any took place, did not reach above this altitude. This is not surprising since ground and aircraft observers did not report any towering cumulus clouds during the aircraft sampling. On the other hand, the difference in the ozone concentrations measured at the beginning and the end of this period increases steadily from the 2600 m level down to the top of the mixed layer. Clearly, vertical transport was occurring, but was limited to the cloud layer, and not above.

FIELD STUDY QA/QC ACTIVITY

The field experiment QA/QC plan was developed as part of the design base document, "VENTEX, Design and Operation Guide for the 1984 Field Study." The plan specified operational, calibration, and data-handling procedures based on ASD-36, the QA Project Plan for the Precipitation Scavenging Module Development Project. This plan and the associated series of Quality Control Descriptors (QCD'S), contain specific procedures for instrument and data activities. This report describes procedures used, results, and deviations from the field operations plan. The following is a summary of the QA/QC report in the project file.

Both airborne and ground-based sampling were employed, with airborne sampling performed by the two PNL aircraft, the Cessna 411 and the DC-3. The

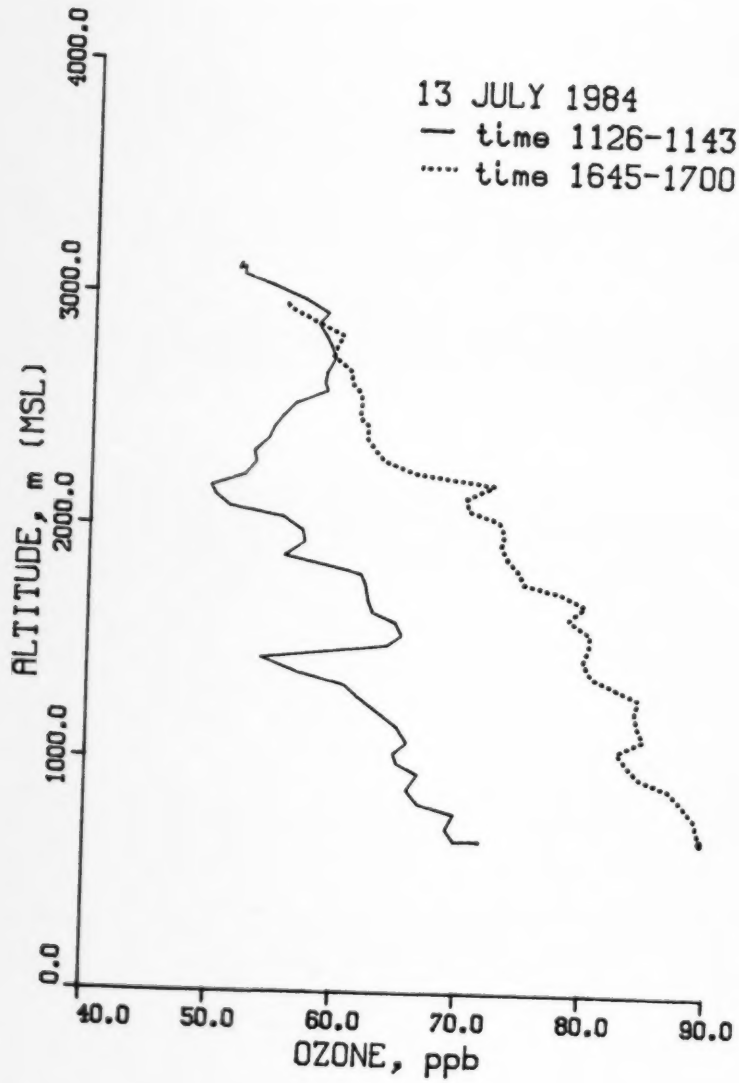

FIGURE 6. Ozone Vertical Profiles for the Morning and Afternoon of July 13, 1984.

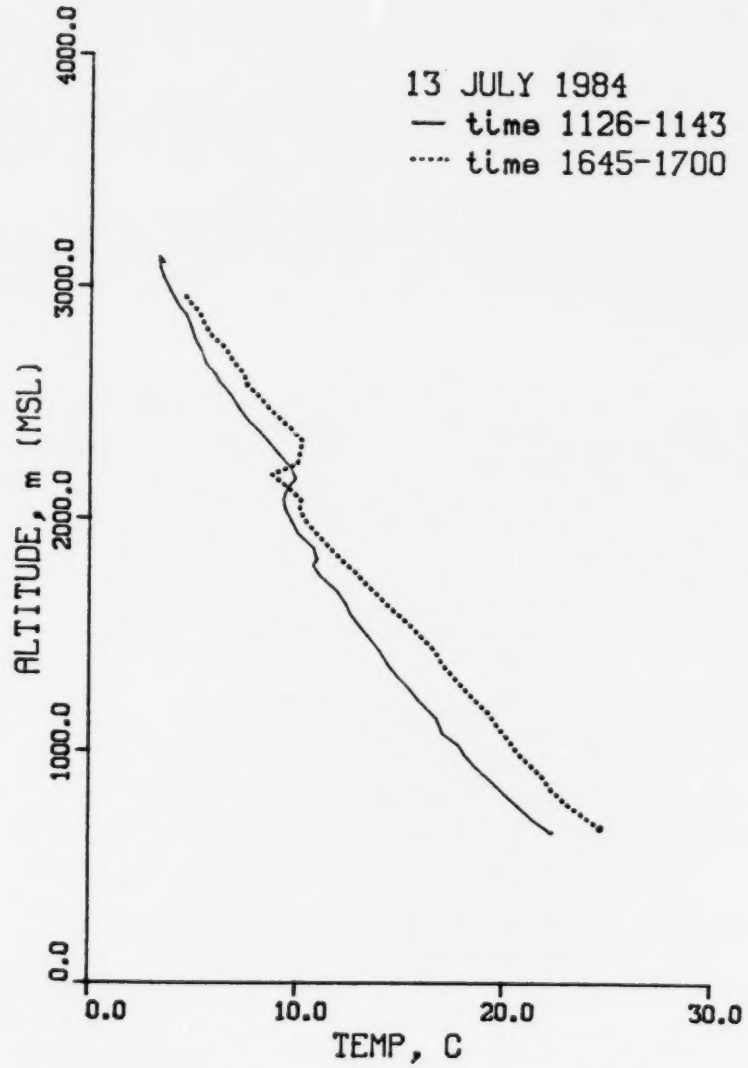

FIGURE 7. Temperature vertical profiled for the morning and afternoon of July 13, 1984.

Cessna 411 flew twice a day for a total of 75.4 hours; the DC-3 flew once a day for a total of 66.2 hours. Table 6 shows the two aircraft flight times and days.

TABLE 6. Aircraft flight log during VENTEX-84.

DATE	DC-3 hrs:min	CESSNA 411 hrs:min	
		Flight 1	Flight 2
7/11		1:55	
7/12		2:40	2:20
7/13		1:30	2:40
7/18		2:30	3:10
7/19		2:35	3:30
7/24		0:40	3:10
7/25	2:00		
7/28	3:50	2:35	1:10
7/29	5:25	4:20	1:30
7/30	5:00		
7/31	5:10		
8/04	5:00	2:25	2:30
8/05	5:50	2:50	2:05
8/06	5:50	2:25	2:00
8/08	5:20	2:30	2:00
8/09	0:25		
8/10	3:00	2:10	
8/12	5:50	2:55	2:15
8/13	5:30	2:45	2:00
8/14		2:05	2:10
8/15	5:20	2:05	2:05
8/16	3:05		

CALIBRATIONS

The primary parameters, associated calibration methods, and schedule are listed in Table 7. Calibration equipment employed in the field included a CSI GPT (Gas Phase Titration) calibrator, AID permeation tube calibrator, flow calibrator, cylinder SRM (Standard Reference Material) gases, FREON 12 and various electronic measurement instruments.

1-Ozone: The Bendix Model 8002 ozone analyzer used in this program has an internal ozone source for routine, daily operational checks. Operation in the zero mode provides a check on the analyzer response to zero gas by passing ambient air through a charcoal scrubber to destroy ozone. Zero and span checks were conducted routinely during operation. The long-term stability of this

unit, confirmed by extensive operating experience on an aircraft platform, made daily multi-point calibration checks unnecessary. Primary calibrations were performed with a CSI 1700 GPT calibrator referenced to a laboratory ozone source. A zero check and four challenge concentrations in the range of 70 to 262 ppb were used. Variations in the instrument response were less than 10% in the range of ambient concentration encountered.

TABLE 7. Instrument calibration methods and schedules.

PARAMETER	METHOD	SCHEDULE
Temperature	NBS Reference Device	1,3
Dewpoint Temp.	NBS Reference Device	1,3
Pressure	NBS Reference Device	1,3
NO_x	Gas-phase titration (SRM NO cylinder)	1,2,3,4
SO_2	SRM Permeation Tube	1,2,3,4
O_3	CSI calibration referenced to UV photometer	1,2,3,4
bscat	Freon 12	1,2,3,4
SF_6	SF_6	1,2,3
Turbulence	Electronic	0,5
Hi-Vol Flow	NBS Reference Device	0,5
Particle Size	Aerosol Generator (latex spheres)	1,3
Position (VLF/INS)	Manufacturer Calibration	4
Wind (INS)	Manufacturer Calibration	4
Air Motion (Gust Probe)	Calibration weights & Electronic	5

Schedule:

0	Primary calibration prior to field deployment
1	Primary calibration before field experiment
2	Primary calibration during field experiment
3	Primary calibration after field experiment
4	Zero and span checks on operating days
5	Primary calibration after return from field

2-Nitrogen Oxides: Quantitative detection of these species is derived from the chemiluminescent reaction between nitric oxide and ozone. The analyzers provide measurement of NO and oxidized nitrogen species which are reduced to NO in a converter prior to entering the reaction chamber. The primary analyzer was constructed at PNL for use in aircraft studies and has a detection limit of less than 1 ppb. Zero checks of NO_x analyzers were conducted

frequently during each flight. Multi-point calibrations for NO and NO_2 were performed prior to, during, and after the field experiment. This procedure utilized a CSI 1700 GPT calibrator and cylinder SRM nitric oxide in nitrogen to check the analyzer response and the NO_x converter operation at zero and four concentrations up to 50 ppb. Instrument response to the calibration standards was determined to be within the 10% specified accuracy for the instrument. Failure of the ozone generator in the NO_x measurement system required replacement by a lower output generator and resulted in some loss of sensitivity for NO_x measurements. Subsequent re-calibrations, however, indicated repeatable response to calibration standard gas for the remainder of the experiment.

3-Sulfur Dioxide: A Meloy flame-photometric analyzer was used to measure airborne concentrations of SO_2. Zero and span checks were performed prior to, during, and after the field study, using a CSI 1700 calibrator and cylinder of SRM SO_2. Instrument operation was less than optimal as a high baseline could not be sufficiently reduced to permit operation on a high sensitivity range, and the instrument had to be operated on the 0 to 100 ppb range. Response to the calibration standard was within the specified 10% accuracy for that range.

4-Light Scattering: An unheated integrating nephelometer, calibrated using Freon 12, was used to measure total light scattering. Daily checks were made using an internal calibration check, and full calibrations with Freon 12 were performed before, during, and after the field study period.

5-Sulfur Hexafluoride: A real-time SF_6 analyzer was installed on the aircraft to detect movement of airborne releases of tracer. Calibrations were performed using SRM cylinder sources of SF_6 gas which was expelled into tedlar bags for sampling at low pressure.

5-Aerosol Size Distribution: Particle characterization instruments were expected to provide qualitative information only and did not undergo rigorous calibration. A TSI 3030 electrical mobility analyzer and an aerosol probe, a PMS ASASP-100X, were operated onboard the DC-3.

6-Meteorological Parameters: Temperature, atmospheric pressure and turbulence instruments were calibrated prior to and after the field study

using NBS traceable instruments. These are reliable, stable sensors which were determined to be within the desired calibration accuracies.

7-Inertial Navigation System/Gust Probe: The INS/gust probe hardware was installed and interfaced to the data acquisition system just prior to the field deployment. INS checkout and gust probe sensor calibration were performed following the field study. Gust probe air vanes are equipped with strain gauges which are calibrated by properly orienting the vanes and applying calibration weights. A differential pressure sensor for monitoring longitudinal airspeed is calibrated by means of an NBS referenced pressure gauge. Data from both systems were recorded via the onboard data acquisition system in the field and will be reduced using post-field calibration data.

DATA HANDLING

It is essential that instrument data are carefully tracked through the total path from instrument to computer data reduction process. Pre-flight, in-flight, and post-flight checks were used to ensure correct operation and data logging. A pre-flight checklist documents several physical checks to be performed, such as power connections, signal connections to the data acquisition system and chart recorders, sample inlet connections, and inventory of required onboard supplies. An in-flight checklist supports examination of instruments for expected operations, with both instrument front panel observations and display of each parameter as received by the data acquisition system, checks for correct operation of instrumentation power conversion and distribution system, chart recorder checks, sample and reagent flow checks, etc.

The DC-3 aircraft acquisition system is a newly installed HP 9920 computer based system which includes an analog-to-digital conversion subsystem, a serial digital interface to the INS and a magnetic tape transport for data recording on 9-track tape. Since the system is programmable, programs can be loaded in the field to permit examination of the data tapes acquired as well as to run the acquisition process, to provide on-the-spot assessment of instrument and data system performance. Calibrated chart recorders were used for checkup and for in-flight indication of experiment progress.

A Particle Measuring Systems probe and acquisition system was also carried on the DC-3 aircraft. Since this system also has analog signal input

capability, several primary parameters were recorded redundantly for backup purposes as well as data quality comparison.

A computer-controlled data acquisition system was used onboard the Cessna 411 aircraft, which recorded data onto 1/4-inch magnetic tape cartridges. This system was also capable of providing field examination of recorded data. Calibrated chart recorders were used to provide backup of primary parameters.

Thirty-one data tapes were acquired during the DC-3 aircraft flights and 30 tapes were recorded on the Cessna 411 aircraft. Backup copies of the raw data tapes were made upon returning to PNL, to be used in the data reduction process. All but 2 of the 30 Cessna tapes were reduced, resulting in estimated data completeness inventory of about 93%. The DC-3 data tapes have not been reduced, only backed up, but with redundant system recording, we expect virtually complete data recovery for all parameters except the inertial navigation system and gust probe data. The INS/gust probe data have gaps as a result of hardware and software problems in the operation of the new data acquisition system. Estimated data recovery for these parameters is 70% to 75%. Table 8 indicates instrument response time, calibration accuracies and estimated data completeness for the aircraft data.

TABLE 8. Accuracy and completeness of the measured parameters during VENTEX-84

Parameter	Instrument Response Time	Accuracy[1]	Accuracy[2]	Completeness[3]
Temperature	2 sec	1°C	1°C	95%
Dewpoint Temp.	0.5 sec/°C	1°C	1°C	93%
Pressure	1 sec	10%	10%	95%
NO_x	3 sec	10%	10%	95%
SO_2	30 sec	10%	10%	95%
Ozone	5 sec	10%	10%	95%
bscat	2 sec	10%	10%	95%
Hi-Vol flow	---	10%	10%	95%
Position	---	10%	10%	70%
Wind	---	10%	10%	(?)
Air motion	---	10%	10%	70%

1 Specified accuracy.
2 Calibration accuracy.
3 Estimated data completeness.

FILTER COLLECTIONS

A primary set of data for this study was obtained from the two high-volume air samplers operated on the DC-3 aircraft; other high-volume samplers were used on the ground. In the aircraft, filter packs were removed from sealed bags and inserted into the high-volume samplers immediately prior to exposure. Upon completion of the sample collection, the filter packs were returned to plastic bags where they remained until transported to the chemistry laboratory no later than the following day. Each filter was marked with a unique identifier and essential information was noted on a collection record as the sample was acquired (ID, time, altitude, volume, sample ID). For each flight, additional filter packs were unsealed and re-bagged to serve as blanks. After disassembly of the packs in the chemistry laboratory, the filters were placed in sterile syringes and leached into solution for analysis. Sample ID and log sheets followed the samples through the analysis and reporting process. Similar procedure was also followed for samples collected on the ground. A total of 37 filter sets were exposed onboard the DC-3 aircraft. Each set consisted of 2 filter packs holding 5 filters. Additionally, 11 sets were handled, but not exposed, to serve as blanks for background correction. On the ground, the number of filters exposed are: 93 for ammonia, 90 for sulfur dioxide filters, 93 for aerosols, and 38 blanks.

Laboratory space for the duration of the field study was provided by the Kentucky Center for Energy Research Laboratory, located north of Lexington, KY. This facility was used as a filter-handling area in which aircraft and surface filter packs were prepared for sampling use and also were unpacked and extracted in preparation for analysis. Filter preparation, particularly those with oxalic acid treatment for capturing ammonia, were completed the day prior or the same day as a planned flight to prevent aging effects and maintain uniform filter collection characteristics.

DEVIATION AND PROBLEMS NOTED

As with any field program, a few difficulties were encountered which affected planned performance. In preparation for the study, a nose boom was constructed for the DC-3 aircraft for mounting of the gust probe components. Problems encountered by the fabricator in securing FAA certification for the

Isaac, G. A., P. I. Joe and P. W. Summers. 1983. "The Vertical Transport and Redistribution of Pollutants by Clouds." Transaction of the APCA Specialty Meeting on the Meteorology of Acid Deposition, ed. P. J. Samson, p. 496. Hartford, Connecticut.

Liu, S. C., J. R. McAfee and R. J. Cicerone. 1984. "Radon 222 and Tropospheric Vertical Transport." J. Geophys. Res., 89:7291.

Maahs, H. G. 1983. "Measurements of the Oxidation Rate of Sulfur(IV) by Ozone in Aqueous Solution and Their Relevance to SO_2 Conversion in Nonurban Tropospheric Clouds." Atmos. Environ., 17:341.

Martin, L. R. and D. E. Damaschen. 1981. "Aqueous Oxidation of Sulfur Dioxide by Hydrogen Peroxide at Low pH." Atmos. Environ.,15:1615.

McDonald, J. E. 1958. "The Physics of Cloud Modification." Adv. Geophys., 5:223.

Nair, S. K., L. K. Peters and A. J. Alkezweeny. 1985. "Formation of Sulfate in Non-Precipitation Clouds." Paper presented at the 78th Annual Meeting of the APCA, June 16-21, 1985, Detroit, Michigan.

Niewiadomski, M. 1986. "A Passive Pollutant in a Three-Dimensional Field of Convective Clouds: Numerical Simulations." Atmos. Environ., 20:139.

Pruppacher, H. R. and Klett. 1958. Microphysics of Clouds and Precipitation, D. Reidel Publishing Company, Boston.

Seigneur, C. and P. Saxena. 1984. "A Study of Atmospheric Acid Formation in Different Environments." Atmos. Environ., 18:2109.

Sellers, W. D. 1974. Physical Climatology, University of Chicago Press, Chicago.

boom resulted in a 2 week delay in getting the aircraft to field site, and even then, it was necessary to place the aircraft in the FAA experimental category designation.

Immediately prior to deployment to the field site, the dewpoint sensor for the DC-3 aircraft was determined inoperational, thus, no dewpoint temperature measurements were made with this aircraft. An operating dewpoint sensor was onboard the Cessna 411 aircraft which was used during the aircraft sampling.

Early in the flight series, the ozone generator for the NO_x monitor failed and had to be replaced with a unit of lower generation capacity. This resulted in some loss of sensitivity for NO_x measurements. As discussed earlier, precalibration results verified acceptable operation.

A high baseline level in the Meloy SO_2 analyzer could not be corrected and also resulted in loss of sensitivity as the instrument had to be operated on a less sensitive range than desirable.

Similarly, baseline problems with the real-time SF_6 analyzer made tracer detection difficult. The few tracer releases that were made were not successful.

Problems also occurred with the data acquisition systems on both aircraft. As discussed earlier, the new DC-3 aircraft computer, INS and gust probe systems were newly installed prior to departure to field site. Difficulties were encountered in intermittent failures in the serial data interface to the INS, but data were recorded for most flights. Hardware/software problems were experienced with the magnetic tape recording system resulting in considerable difficulty in maintaining a continuous acquisition and recording process. For most flights, there were frequent short time interruptions in recording. Also, due to limited time with the system prior to departure to the field site, on-site analysis of the recorded data was not attempted. Dump programs were used to ensure that data was being correctly recorded on a daily bases.

The microprocessor acquisition system on the Cessna 411 aircraft also experienced intermittent failures. Fortunately, these were physical interconnect problems which were generally corrected prior to the aircraft takeoff. Two tape cartridges recorded on this system were found to be defective; one with loss of data and one which internally jammed in-flight.

Only one sampling mission was cancelled as a result of aircraft problems. An August 14 flight had to be scrubbed when a defective fuel boost pump was discovered on the DC-3 aircraft left engine. Repairs were completed in time for flight the following day. Other scheduled aircraft maintenance was performed as planned.

SUMMARY

Preliminary results show that the ratio of sulfate concentration to the total sulfur concentration (the sum of sulfate and sulfur dioxide) at top of clouds is much higher than that measured at their bases. The in-cloud oxidation rates were calculated to be in excess of 100%/hr. This required an assumed averaged updraft velocity of 1.0 m/sec. The ratio of the total nitrate concentration (the sum of nitric acid and nitrate aerosols) to the total sulfur concentration at cloud tops, was higher than that at cloud bases on many days. This result suggests that nitrate can form in the clouds but not as frequently as sulfate.

The ammonia concentrations measured on the ground show a decline around midday followed by recovery in the afternoon. On the other hand, the sulfur dioxide concentrations show an opposite trend for the one day that was examined, August 12, 1984.

The vertical profiles of ozone measured during the morning and afternoon of July 13, 1984 indicated that pollutants from the mixed layer have been transported vertically to the cloud layer. No transport above the layer was detected on this day. It should be noted that no towering cumulus clouds were observed during the aircraft sampling.

REFERENCES

Alkezweeny, A. J., W. E. Davis, and R. C. Easter. 1980. "Comparison of Ozone in Polluted and Clean Air Masses Over Lake Michigan." In Proceedings of the International Ozone Symposium, August 4-9, 1980, Boulder, Colorado. Vol. 1, ed. Julius London.

Alkezweeny, A. J. and J. M. Hales. 1981. "The Impact of Non-Precipitating Clouds on the Transport and Formation of Acid Aerosols." Paper presented at the Annual Meeting of the American Chemical Society, August 1981, New York, New York.

Alkezweeny, A. J. 1984. Non-Precipitating Cumulus Cloud Study. PNL-5283, Pacific Northwest Laboratory, Richland, Washington.

Alkezweeny, A. J., K. M. Busness, and D. W. Koppenaal. 1984. "Contribution of Non-Precipitating Clouds to Acid Deposition." Paper presented at the Fourth Joint Conference on Application of Air Pollution Meteorology, October 1984, Portland, Oregon.

Alkezweeny, A. J., G. L. Laws, and W. Jones. 1986. "Aircraft and Ground Measurements of Ammonia in Kentucky." Atmos. Environ., 20:357.

Ching, J. K. S., J. F. Clarke, J. M. Irwin, and J. M. Godowitch. 1983. "Relevance of the Mixed Layer Scaling for Daytime Dispersion Based on RAPS and Other Field Programs." Atmos. Environ., 17:859.

Ching, J. K. S., and A. J. Alkezweeny. 1985. "Vertical Transport by Cumulus Clouds." Paper presented at the 7th Symposium on Turbulence and Diffusion of the AMS, November 12-15, 1985.

Clark, P. A., I. S. Fletcher, A. S. Kallend, W. J. McElroy, A. R. W. Marsh, and A. H. Webb. 1984. "Observations of Cloud Chemistry During Long-Range Transport of Power Plant Plumes." Atmos. Environ., 18:1849.

Calvert, J. G. and W. R. Stockwell. 1983. "Acid Generation in the Troposphere by Gas-Phase Chemistry." Environ. Sci. Tech., 17:428A.

Eatough, D. J., R. J. Arthur, N. L. Eatough, M. W. Hill, N. F. Mangelson, B. E. Richter, L. D. Hansen, and J. A. Cooper. 1984. "Rapid Conversion of $SO_2(g)$ to Sulfate in a Fog Bank." Environ. Sci. Tech., 18:855.

Gillani, N. V., J. A. Colby, and W. E. Wilson. 1983. "Gas-to-Particle Conversion of Sulfur in Power Plant Plumes-III. Parameterization of Plume-Cloud Interactions." Atmos. Environ., 17:1753.

Hegg, D. A. and P. V. Hobbs. 1982. "Measurements of Sulfur Production in Natural Clouds." Atmos. Environ., 16:2663.

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